

## Article

# (Perylene)<sub>3</sub>-(TCNQF<sub>1</sub>)<sub>2</sub>: Yet Another Member in the Series of Perylene–TCNQF<sub>x</sub> Polymorphic Charge Transfer Crystals

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**Abstract:** The 3:2 Charge Transfer (CT) co-crystal (Perylene)<sub>3</sub>(TCNQF<sub>1</sub>)<sub>2</sub> is grown by the Physical Vapor Transport (PVT) method, and characterized structurally and spectroscopically. Infrared analysis of the charge sensitive modes reveals a low degree of charge transfer (less than 0.1) between donor and acceptor molecules. The crystal is isostructural to the other 3:2 CT crystals formed by Perylene with TCNQF<sub>2</sub> and TCNQF<sub>4</sub>, whereas such stoichiometry and packing is not known for the CT crystals with non-fluorinated TCNQ. The analysis of the isostructural family of 3:2 Perylene–TCNQF<sub>x</sub> (x = 1,2,4) co-crystal put in evidence the role of weak F⋯HC bonding in stabilizing this type of structure

**Keywords:** charge transfer crystals; X-ray diffraction; vibrational spectroscopy

## 1. Introduction

Recently, the study of charge transfer (CT) crystals has been reinvigorated by its potential applications in organic electronics [1,2], due to the possibility of having both *n*- and *p*-type behaviors in organic field effect transistors (OFETs) [3–5]. The CT interaction between the frontier  $\pi$ -orbitals of the electron Donor (D) and Acceptor (A) molecules is generally the predominant intermolecular interaction in a solid state, so that many properties, including mobility, have strong directional characters. The packing is indeed characterized by the presence of stacking of the involved  $\pi$ -molecules, hence, the name of “quasi 1-dimensional” crystals for these systems.

Because of the focus on the role of the CT interaction, the occurrence of polymorphism in CT crystals has been sort of neglected, at least in comparison with one-component  $\pi$ -molecular semiconductors [6]. However, the above mentioned increased research activity in the field of CT crystal, polymorphism and its effect on the physical properties have started to emerge, even for the prototypical ambipolar system DBTTF-TCNQ [7,8]. As a matter of fact, the family of co-crystals made up of Perylene and F-substituted Tetracyanoquinodimethane (TCNQF<sub>x</sub>) exhibits such a large variety

of different packings and stoichiometry as to be considered as a paradigmatic example of the old sentence: “the number of forms known for a given compound is proportional to the time and energy spent in research on that compound” [9]. Three different polymorphs with 1:1 ratio of D to A ( $\alpha$ ,  $\beta$  and  $\gamma$ ) are known for the crystals formed by Perylene with unsubstituted TCNQ [10], accompanied by two “stoichiomorphs” with 2:1 and 3:1 composition [11,12]. Perylene and TCNQF<sub>2</sub> form two types of crystals, with 1:1 and 3:2 stoichiometry. In addition to these two stoichiometries, TCNQ<sub>4</sub> also forms a solvated CT crystal with the inclusion of toluene [13]. This wide variety of packings allows one to try to correlate physical properties with the packing motif [11,14], and suggests that the role of crystal engineering in building up the CT co-crystals with the desired properties is not limited to the choice of the D/A pair with the proper ionization potential and electron affinity, but that other types of intermolecular interactions have to be taken into account.

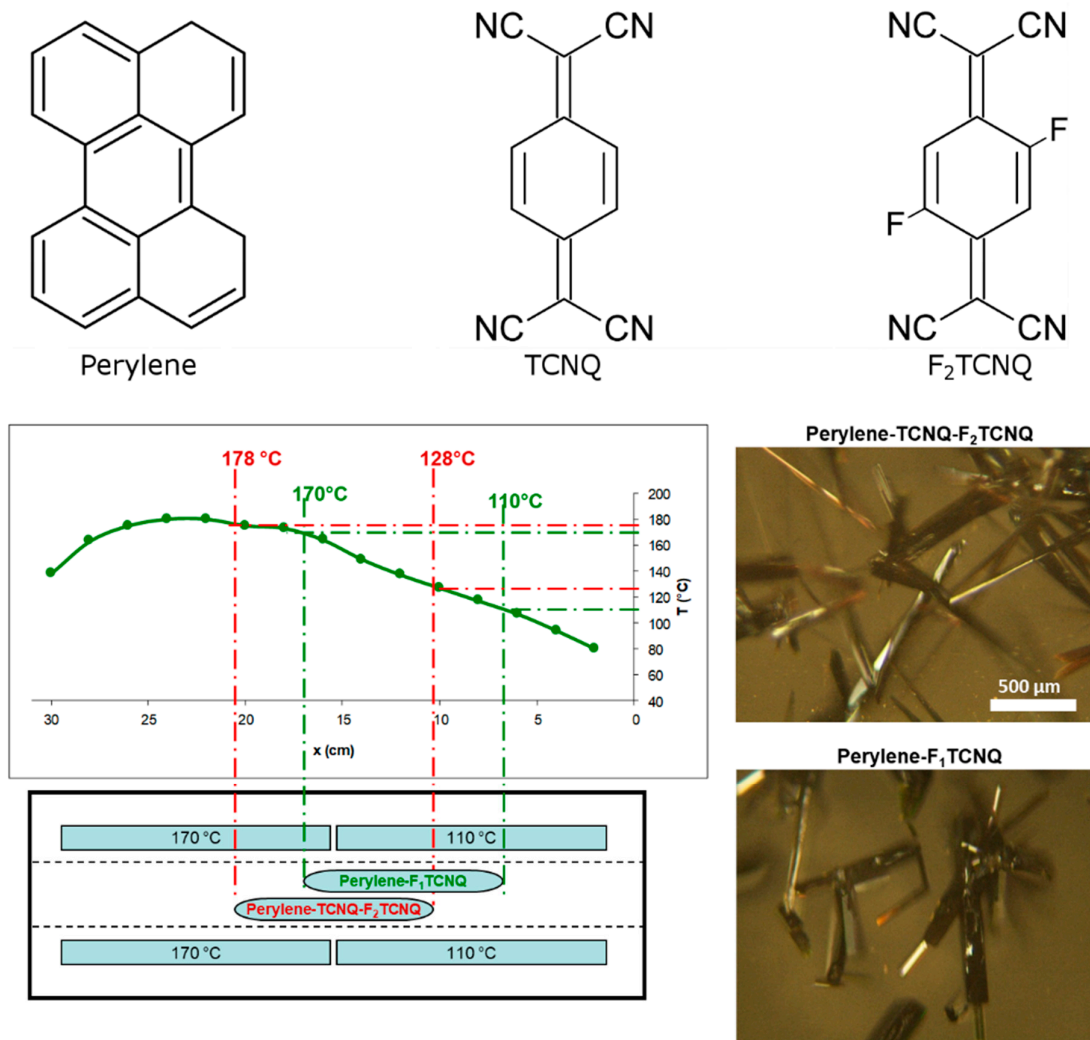
In this paper we present the structural and spectroscopic characterization of a 3:2 CT crystal of Perylene–TCNQF<sub>1</sub>, which adds to the already known 1:1 system [15]. This new system is isostructural to (Perylene)<sub>3</sub>–(TCNQF<sub>2</sub>)<sub>2</sub> and to (Perylene)<sub>3</sub>–(TCNQF<sub>4</sub>)<sub>2</sub> [13], so that all the three F-substituted TCNQs give rise to two different co-crystals with 1:1 and 3:2 D/A ratio, while no 3:2 co-crystals of Perylene with unsubstituted TCNQ are known. We also report on the attempt to include TCNQ in a 3:2 system together with TCNQF<sub>2</sub>. Analysis of the structures of the three 3:2 Perylene–TCNQF<sub>x</sub> CT crystals allowed us to underline the role of the weak F...HC bonding in stabilizing this type of packing.

## 2. Materials and Methods

### 2.1. Sample Preparation and Crystal Growth

Perylene (Sigma Aldrich (St. Louis, Missouri, USA), purity 99%), TCNQ (Sigma Aldrich, purity 98%), TCNQF<sub>1</sub> (Tokyo Chemical Industry (Tokyo, Japan), purity 98%) and TCNQF<sub>2</sub> (Tokyo Chemical Industry, purity 98%) were used as purchased. All solvents (from Aldrich (St. Louis, Missouri, USA)) were of spectroscopic grade. The single crystals of the binary system Perylene–TCNQF<sub>1</sub> and of the supposedly ternary system Perylene–TCNQF<sub>2</sub>[TCNQ] were obtained by the Physical Vapor Transport (PVT) method. A quartz ampoule of 100 mm length and 10 mm diameter was cleansed with soap, distilled water, isopropanol and acetone, in this order, and then left to dry overnight at 110 °C. For the crystal growths, the ampoule was loaded with equimolar amounts of the parent compounds, namely, Perylene and TCNQF<sub>1</sub> in the first case, and Perylene, TCNQ and TCNQF<sub>2</sub> in the second case. The ampoule was then evacuated in N<sub>2</sub> to a final pressure of 10<sup>−4</sup> mbar, sealed with an oxygen-natural gas burner, and placed in a two-zone furnace. For Perylene–TCNQF<sub>1</sub>, the temperature was set at 170 °C and 110 °C at the hot and cold end of the apparatus, respectively; for Perylene–TCNQF<sub>2</sub>[TCNQ], temperatures of 178 °C and 128 °C were selected for the same setup (see Figure 1).

The potassium salt of TCNQF<sub>1</sub> (K<sup>+</sup> TCNQF<sub>1</sub><sup>−</sup>) was prepared following the experimental procedure described by Melby et al. [16], using the reaction of the iodide with TCNQF<sub>1</sub>. When the hot solutions of potassium iodide and TCNQF<sub>1</sub> in acetonitrile were mixed, the potassium salt precipitated as a dark purple crystalline solid with a needle-like morphology. TCNQF<sub>1</sub> and potassium iodide were mixed in ratio 2:3 using the excess of metal iodide to scavenge the iodine by-product as I<sup>−</sup>.



**Figure 1.** Chemical formulas (top), scheme of the PVT crystal growth technique (bottom left), and photographs of the grown crystals (bottom right).

## 2.2. X-Ray Diffraction Measurements

Single crystal diffraction data for the Perylene-TCNQF<sub>1</sub> and Perylene-TCNQF<sub>2</sub>[TCNQ] 3:2 structures were collected at 150 K on a Nonius Kappa CCD diffractometer (Netherlands) with graphite mono-chromated Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å. Unit cell determination, data scaling, and corrections for Lorentz and polarization effects were performed with Denzo-SMN [17]. A symmetry-related (multi-scan) absorption correction was applied. Structure solution, followed by full-matrix least-squares refinement, was performed using the WINGX-v2014.1 [18] suite of programs throughout. Hydrogen atoms were placed onto calculated positions and refined using a riding model. Crystallographic data for the reported structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC), reference numbers CCDC 1963867 and 1963868.

## 2.3. Spectroscopic Measurements

Infrared (IR) spectra of the CT crystals were recorded with a Bruker IFS66 (Ettlingen, Germany). Fourier transform IR (FT-IR) spectrometer coupled to an IR microscope Hyperion 1000. The spectrometer is equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The instrument setup allows for reflection and transmission measurements with polarized light.

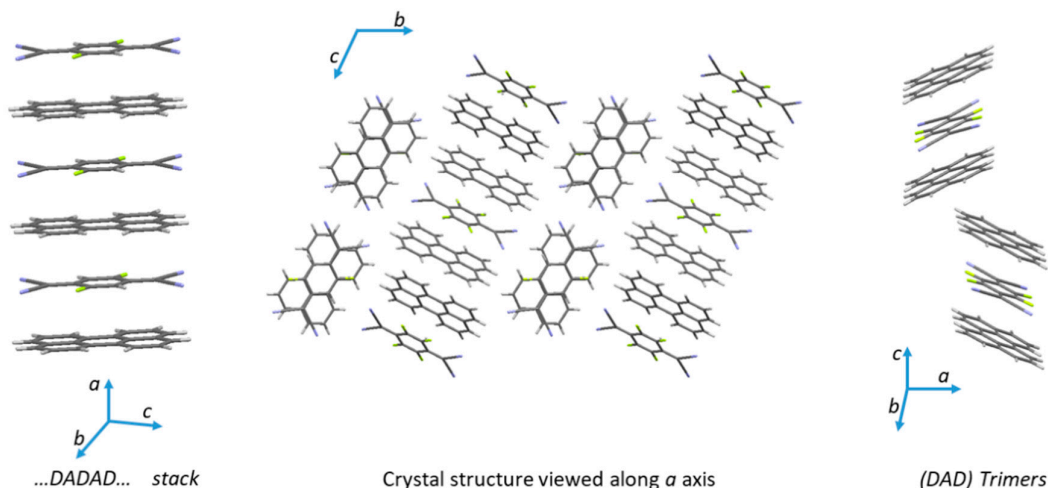
The Raman spectra were recorded with a Horiba Jobin Yvon T64000 triple gratings Raman spectrometer equipped with the appropriate interferential filter and coupled to an Olympus BX40 microscope (Shinjuku, Tokyo, Japan) with 50× or 100× objectives. The 647.1 nm excitation line from a Krypton ion (Kr+) laser was used as light source, wavelength long enough to prevent fluorescence emission of the studied systems.

### 3. Results

#### 3.1. Crystal Structure

The binary system Perylene–TCNQF<sub>1</sub> obtained by the PVT method in an open tube using inert gas as carrier transport is known to crystallize in a monoclinic structure with mixed stack DA arrangement in a 1:1 ratio [15]. By growing the crystals by PVT in a closed ampoule (see Section 2.1) we obtain the Perylene–TCNQF<sub>1</sub> stochiomorph in a 3:2 D/A ratio. This CT crystal crystallizes in the triclinic space group P-1 and is characterized by a slightly dimerized ...DADAD... stack along the *a*-axis and trimeric (DAD) units arranged in a zig-zag pattern along the *c*-axis (Figure 2). The crystal is isostructural to the other two 3:2 CT crystals formed by Perylene with TCNQF<sub>2</sub> and TCNQF<sub>4</sub>, also grown by PVT in closed ampoule [13]. A comparison of the basic structural parameters of the three CT crystals is given in Table 1.

The slightly dimerized stack displays an average D–A distance of 3.32 Å and an intrinsic disorder of the F atoms. The F occupancy was refined up to the best R value, then it was kept fixed in the final stage to avoid non-integer numbers, with practically no change in the R value. We get 80% overall occupancy factor in positions 2 and 5 of the TCNQ ring. The DAD trimers are arranged quasi perpendicularly to the ...DADAD... stack, with the TCNQF<sub>1</sub> molecules residing on inversion center, with a random disorder of the F atoms, approx. 25% of occupancy on each position. The average D–A distance within the trimers (3.26 Å) is considerably shorter than that in the stacks. Furthermore, the trimeric units display a tilted angle between the Perylene units of 48.33°.



**Figure 2.** Crystal structure of (Perylene)<sub>3</sub>-(TCNQF<sub>1</sub>)<sub>2</sub>.

**Table 1.** Basic structural parameters of the three isostructural CT crystals Perylene–TCNQF<sub>x</sub> 3:2.

	TCNQF <sub>1</sub> <sup>1</sup>	TCNQF <sub>2</sub> <sup>2</sup>	TCNQF <sub>4</sub> <sup>2</sup>
Stoichiometry	3:2	3:2	3:2
Space group	P-1	P-1	P-1
Temperature (K)	150(2)	150(2)	150(2)
<i>a</i> (Å)	7.2254(2)	7.2307(1)	7.2066(2)
<i>b</i> (Å)	19.1275(4)	19.1407(3)	19.0974(6)
<i>c</i> (Å)	22.3203(6)	22.2723(5)	22.4050(7)

$\alpha(^{\circ})$	112.2658(14)	112.2834(8)	111.8014(14)
$\beta(^{\circ})$	90.2346(10)	90.1900(8)	90.0472(17)
$\gamma(^{\circ})$	94.0322(15)	93.7599(12)	94.1283(17)
$V(\text{\AA}^3)$	2846.09(13)	2844.85(9)	2854.3(15)
Z	2	2	2
Final $R^{[a,b]}$ indices $[I > 2\sigma(I)] / wR2$	0.0722 / 0.1948	0.0966 / 0.2189	0.104 / 0.2804

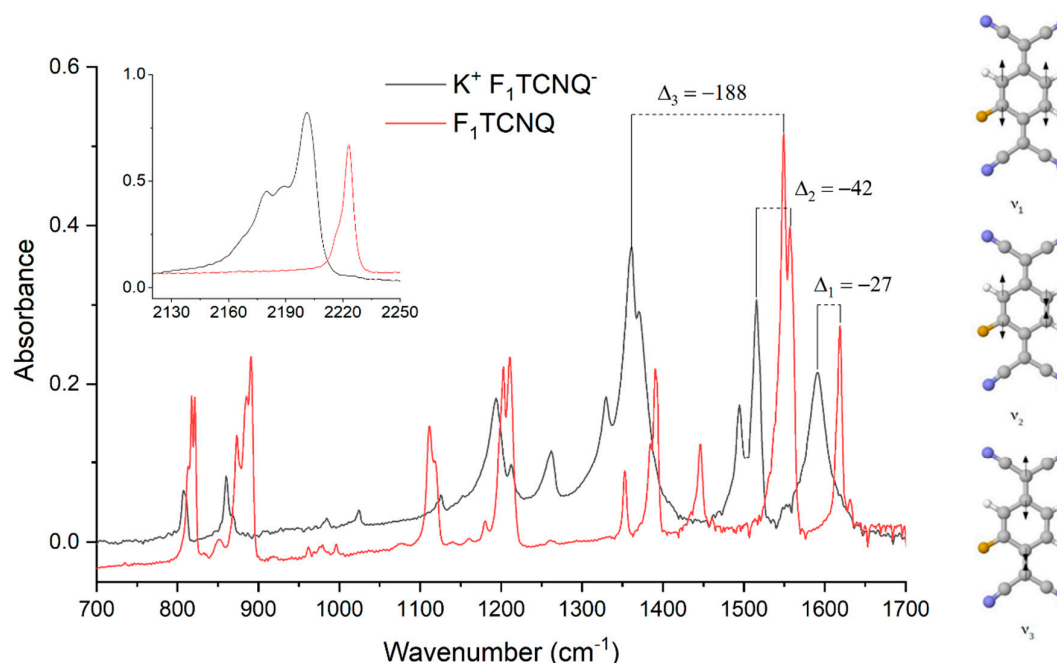
[a]  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , [b]  $wR2 = \{\sum [w(F_o2 - F_c2)^2] / \sum [w(F_o2)^2]\}^{1/2}$  <sup>1</sup> This work. <sup>2</sup> From Ref. [13].

We have also attempted to obtain a ternary crystal made by the combination of Perylene with a 1:1 mixture of TCNQ and TCNQF<sub>2</sub>. The crystal is isostructural to the just examined 3:2 Perylene–TCNQF<sub>x</sub>, but the X-ray analysis did not show clear evidence of the presence of the non-fluorinated TCNQ. The refinement gave an acceptable R-factor by assuming that the crystal was actually twinned, and we obtained only a slight improvement to the final R of 10.4 % by also assuming that some TCNQ goes into the DADAD stack, whereas its presence in the trimers is very dubious. The final structural parameters (CCDC 1963868) are the same, within the experimental error, as those of pure (Perylene)<sub>3</sub>(TCNQF<sub>2</sub>)<sub>2</sub> (Table 1), and also the spectroscopic measurements did not show evidences of TCNQ. We conclude that non-fluorinated TCNQ, at most, enters the crystal as an impurity, so that we label the system as 3:2 Perylene–TCNQF<sub>2</sub>[TCNQ], and shall not discuss it anymore here.

### 3.2. Determination of the Degree of CT

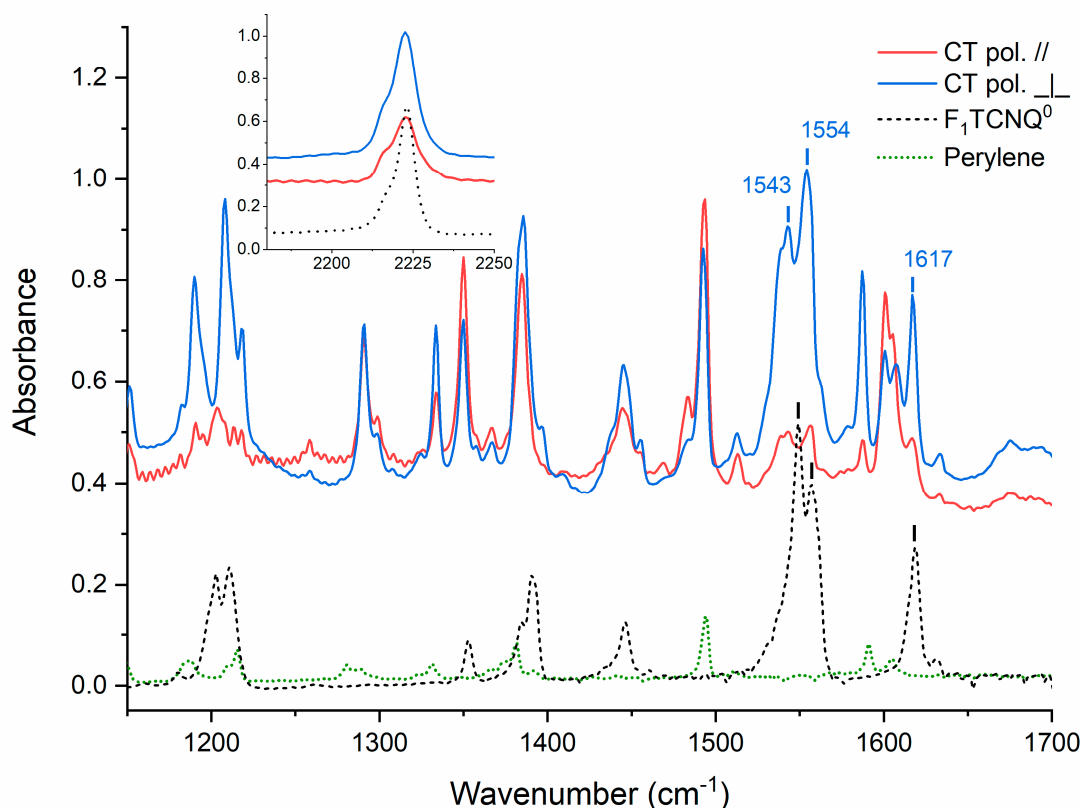
One of the key parameters characterizing the ground state properties of CT crystals is the ionicity, i.e., the degree of charge transfer from D to A. The degree of CT essentially depends on the donor/acceptor characteristics of the molecular components, i.e., the ionization potential and the electron affinity, and on the packing arrangement inside the crystal, which affects the Madelung energy. Therefore, if like in the present case, we have a series of isostructural crystals with differently fluorinated TCNQF<sub>x</sub> having increasing electron affinities, we expect to find increasing  $\rho$  values. Vibrational spectroscopy is a well-established method to estimate the degree of charge transfer in CT crystals by looking at the frequencies of the so-called “charge sensitive” vibrational modes, i.e., the modes with frequencies strongly affected by the charge residing on the molecular site [19,20]. Such modes must be singled out by studying the vibrational spectra of the neutral and fully ionic molecule. Raman is not reliable for mixed stack CT crystals like the present ones, as the frequencies of totally symmetric modes may be affected by the coupling with the CT system [19,20]; thus, we shall limit ourselves to examining the only IR active modes in detail.

Since the strong acceptor TCNQ skeleton is easily ionized, the determination of  $\rho$  in binary systems is generally based on its charge sensitive modes. These have been already identified for TCNQ, TCNQF<sub>2</sub> and TCNQF<sub>4</sub> [13] and references therein]. Instead, to the best of our knowledge, a detailed study of TCNQF<sub>1</sub> vibrations is still missing, even though this molecule is increasingly used in the formation of CT crystals [21]. For this reason, the details of the analysis are given here. To identify the charge sensitive modes of TCNQF<sub>1</sub> we have measured the IR absorption spectra of the neutral molecule and its anion TCNQF<sub>1</sub><sup>−</sup> in the K<sup>+</sup> TCNQF<sub>1</sub><sup>−</sup> salt. The spectra are reported in Figure 3. The full analysis and the assignment of the IR spectra have been carried out with the help of quantum chemical calculations, the details of which are reported in the Supplementary Materials. In Table S1, we report the harmonic frequencies, infrared intensities and normal mode eigenvectors of the most important vibrational modes calculated by the DFT method using the B3LYP hybrid functional and 6.31G(d,p) basis set for both neutral and ionic TCNQF<sub>1</sub>.



**Figure 3.** IR absorption spectra of TCNQF<sub>1</sub> and K<sup>+</sup>TCNQF<sub>1</sub><sup>-</sup> powders (left) and schematics of the charge sensitive vibrational modes (right).

The three vibrational bands marked in Figure 3 with full vertical lines have been found to show the largest ionicity frequency shifts ( $\Delta$ ) for the TCNQF<sub>1</sub> molecule. In terms of their harmonic eigenvectors, modes  $v_1$  and  $v_2$  correspond to the in-phase and the out-of-phase stretching of the two C=C bonds of the TCNQ ring, while mode  $v_3$  can be described as the anti-symmetric stretching of the two apical C=C bonds (see Figure 3). However, while the  $v_1$  and  $v_2$  bands can be safely assigned in the spectra of neutral (1618 cm<sup>-1</sup> and 1557 cm<sup>-1</sup>) and ionic TCNQF<sub>1</sub> (1591 cm<sup>-1</sup> and 1515 cm<sup>-1</sup>), the  $v_3$  band, occurring at 1549 cm<sup>-1</sup> in the spectrum of the neutral molecule, shift down to 1361 cm<sup>-1</sup> upon ionization, crossing several other vibrational modes and slightly altering its eigenvector description. Therefore we do not expect [22] that it will exhibit the linear dependence on  $\rho$  necessary to estimate the degree of CT in case of intermediate ionicity. For analogous reasons, we exclude the C≡N antisymmetric stretching modes (inset of Figure 3), which also show appreciable ionicity frequency shift, but are potentially affected by the molecular environment like electrostatic potential, hydrogen and halogen bonding [23,24]. In the estimate of  $\rho$  for CT crystals involving TCNQF<sub>1</sub> we mainly rely on the  $v_1$  and  $v_2$  modes, exhibiting an ionicity red-shift of 27 cm<sup>-1</sup> and 42 cm<sup>-1</sup>, respectively, and use the  $v_3$  as a consistency check.



**Figure 4.** Polarized IR absorption spectra of Perylene–TCNQF<sub>1</sub> 3:2 CT crystal.

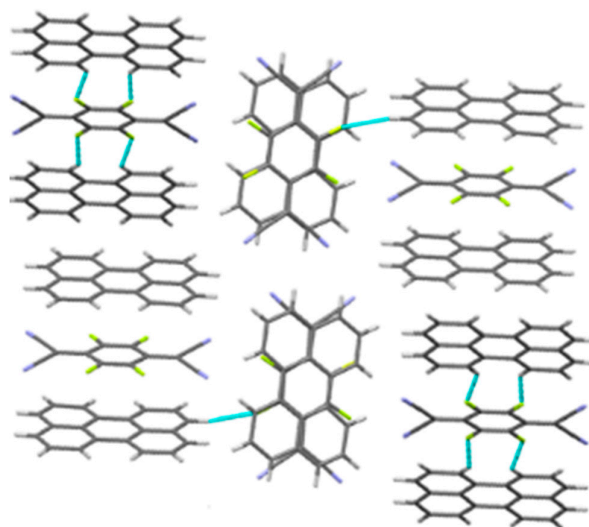
In Figure 4 we report the IR absorption spectra of the (Perylene)<sub>3</sub>–(TCNQF<sub>1</sub>)<sub>2</sub> CT crystal polarized along two mutually perpendicular directions, one with the electric vector along the *a*-axis, namely, along the ...DADAD... stack (red curve), and the other perpendicular to it (blue curve), namely, along the alignment direction of the (DAD) trimers. In the latter spectrum, we then observe the in-plane modes of the molecules within the stack, and we single out the three above-mentioned charge sensitive bands occurring at 1617, 1554 and 1543 cm<sup>−1</sup>, which are only slightly shifted with respect to the bands of the neutral TCNQF<sub>1</sub> (Figure 3 and dashed black line in Figure 4). The position of these bands yields an estimate of *p* of 0.04 and 0.09 for the *v*<sub>1</sub> and *v*<sub>2</sub> modes, respectively, and 0.03 for the less reliable *v*<sub>3</sub> mode. We conclude that the degree of CT is very small in the 3:2 Perylene–TCNQF<sub>1</sub> crystal, with an estimate of *p* below 0.1, very similar to the 1:1 Perylene–TCNQ stoichiomorph [13]. Raman spectra also confirm the slight ionicity of the system as for the small shift of the *v*<sub>R</sub>(C=C) vibration at about 1459 cm<sup>−1</sup> of the neutral TCNQF<sub>1</sub> (see Supplementary Materials, Figure S1). We conclude that the addition of just one F atom to the TCNQ skeleton does not increase the degree of CT appreciably with respect to the non-fluorinated TCNQ.

#### 4. Discussion and Conclusions

The Perylene–TCNQF<sub>1</sub> 3:2 structure presented here completes the series of CT crystals formed by Perylene with TCNQF<sub>*x*</sub>, in the sense that all the co-crystals containing fluorinated TCNQ crystallize either in a stacked structure ...DADA... with D/A 1:1 ratio, or in isostructural 3:2 co-crystals where the stack is accompanied by (DAD) lateral trimers. As we have already noted in the Introduction, Perylene forms with TCNQ several CT co-crystals, with 1:1, 2:1 and 3:1 DA ratios [10,11,13,15,25,26], but none with the 3:2 ratio and the associated triclinic packing. Furthermore, the attempt to insert non-fluorinated TCNQ into the 3:2 structure of TCNQF<sub>2</sub> essentially failed; although it may be related to growth conditions, different sublimation temperatures etc. Finally, in our



experience, the 1:1 co-crystal Perylene–TCNQF<sub>1</sub> is obtained more easily than the 3:2 reported here for the first time, but the opposite is true for Perylene–TCNQF<sub>4</sub> [13], whereas in the case of Perylene–TCNQF<sub>2</sub> in solution, an equilibrium is established between the two stoichiomorphs [27].



**Figure 5.** Structure of (Perylene)<sub>3</sub>(TCNQF<sub>4</sub>)<sub>2</sub> viewed along the *a*-axis. F...H contacts are evidenced in turquoise.

The above empirical observations suggest that the 3:2 packing is favored by the presence of F atoms. A hint of the reason is given by the fact that in the 3:2 structure of both TCNQF<sub>1</sub> and TCNQF<sub>2</sub>, the F atoms of the stacked TCNQF<sub>x</sub> preferentially occupy the 2,5 position. By looking at the structure (Perylene)<sub>3</sub>(TCNQF<sub>4</sub>)<sub>2</sub> in Figure 5 we indeed notice that within the ...DADAD... stack, only the F atoms in 2,5 positions have short contact with the Perylene trimers. There are also short F...HC inter-trimer contacts, so as to stabilize 2-dimensional lateral trimer networks, but in this case, all the four F positions are equally involved.

The present study demonstrates that the F atoms not only increase the TCNQ electron affinity, but also have an active role in the crystal packing through F...H bonds. The importance of halogen bonding is of course well known in crystal engineering, although the role of weak intermolecular bonding involving F and HC is still an active matter of study [28]. Here, we have an example of the interplay of F...HC intermolecular bonding with 1-dimensional CT interaction that favors the face-to-face molecular arrangement of the  $\pi$ -molecules. We believe that such CT/F...HC interplay is worth further investigation, as fluorinated molecules are making their way in the field of organic materials, where proper crystal engineering is of vital importance [29].

**Supplementary Materials:** The following are available online at [www.mdpi.com/2073-4352/10/3/177/s1](http://www.mdpi.com/2073-4352/10/3/177/s1), Table S1. Frequencies, eigenvectors and infrared intensities of the most important vibrational modes; Figure S1. Raman spectra of the neutral TCNQF<sub>1</sub> (black), Perylene (green), potassium TCNQF<sub>1</sub> salt (red) and of the charge transfer complex TCNQF<sub>1</sub>-Perylene (blue).

**Author Contributions:** Conceptualization, T.S.; Data curation, M.M. and G.K.; Methodology, A.B.; Writing – original draft, A.G.; Writing – review & editing, R.G.D.V., E.V. and D.D.N. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest



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